

Docket No.: 0315-0158PUS1  
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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In re Patent Application of:  
Antonio Luiz Duarte BRAGANÇA et al.

Application No.: 10/518,443

Confirmation No.: 7833

Filed: July 1, 2005

Art Unit: 1755

For: SOLID CATALYST COMPONENT FOR  
POLYMERIZATION AND  
COPOLYMERIZATION OF ETHYLENE,  
AND, PROCESS FOR OBTAINING THE  
SAME

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Examiner: J. E. McDonough

DECLARATION OF COMMERCIAL SUCCESS

MS AMENDMENT  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

I, Dr. Márcia S. Lacerda Miranda, residing c/o R. Dr. Barbosa Goncalves, 680 – Chácara das Pedras 91330-320 Porto Alegre/RS, Brazil do declare and say as follows:

I am one of the inventors of U.S. Patent Application Serial No. 10/518,443 filed on December 20, 2004, entitled "Solid Catalyst Compounds for Polymerization and Copolymerization of Ethylene, and Process for Obtaining the Same."

The patent application has been assigned to BRASKEM S.A. of Brazil. Braskem is a Brazilian petrochemical company and the thermoplastic's production leader in Latin America. It has become one of the five largest private industrial companies in Brazil with an annual

production of 1,154 K ton of polyethylene. Linear low density polyethylene (LLDPE) is one of the thermoplastics produced by Braskem and its annual production is about 360 K ton.

For the Examiner's perusal, the Applicants have attached to the present Declaration, as Appendix I, a general market analysis which points out the market significance of polyethylene, particularly High Density Polyethylene (HDPE) and LLDPE as defined by the Applicants' inventive contribution. With this market analysis in mind, it is understandable that what, at first glance, might be considered as small improvements in a catalyst composition, associated processes and products made therefrom, such as for example, the use of lower amounts of titanium, magnesium and chlorine in the catalyst system, a polymer with good morphology, a bulk density of 0.36 or greater, a low amount of fines in the polymer, and the like, in fact reflects significant financial benefits with the ability to produce high quality products at considerable financial savings.

It is precisely for the above reasons that Braskem, the assignee of the present application, has been negotiating with both BASF of Germany and WR Grace of the United States as possible partners in the polyethylene business, utilizing the technology defined by the present invention. Thus, BASF, has agreed to produce the Braskem catalyst system which Braskem will use in their polymerization pilot plant from February to April 2008.

With respect to WR Grace, a meeting has been planned for January 2008 to discuss providing a large amount of catalyst for pilot plant tests. Braskem will choose either BASF or

WR Grace as a long term commercial partner. The selected company will provide Braskem with between 30 and 50 tons off catalyst per year for use in one of Braskem's polyethylene plants, which produces about 300 K ton/year of polyethylene, with the plan to expand polyethylene production to a number of polyethylene plants both in Brazil and abroad. Clearly all of the above activities have already required considerable expenditures by all parties based upon a very high likelihood and expectation of commercial success.

More specifically, Appendix 2 attached hereto shows that 1.6 million has already been spent to date in development costs associated with the present invention with future pilot plans and industrial tests costing about 3 million.

I the undersigned, Dr. Miranda, was present at the interview conducted with Examiner and his Supervisory Examiner and I am a major player in the commercialization of the invention of the present application.

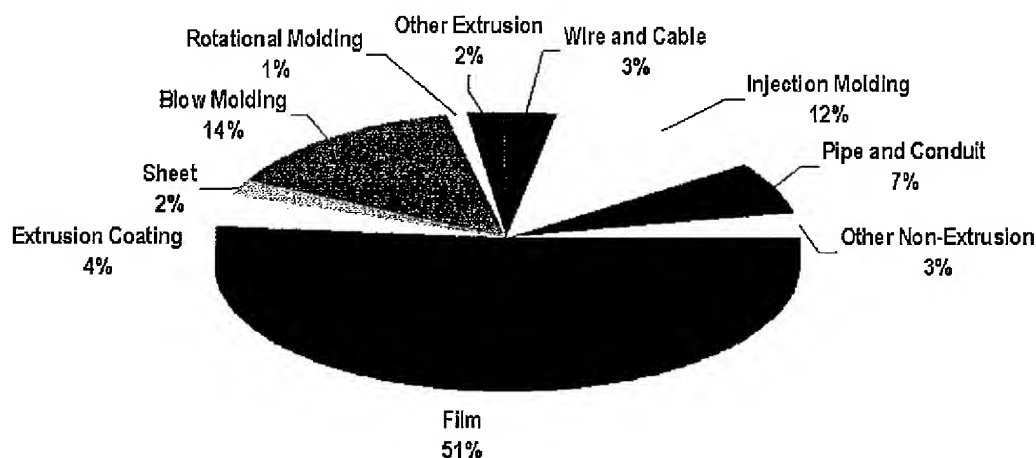
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

January 8<sup>th</sup>, 2008  
Date

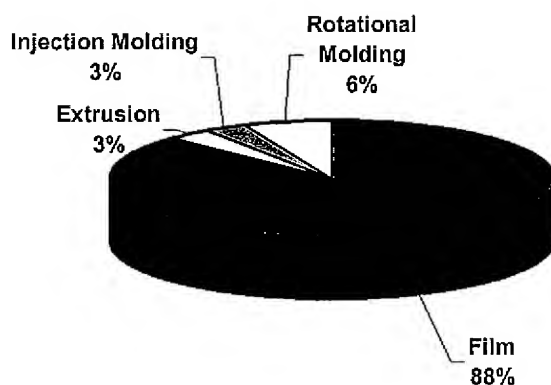
Marcia S. Lacerda Miranda  
Dr. Marcia S. Lacerda Miranda

**APPENDIX 1****FINAL REPORT****PATENT APPLICATION Serial No. 10/518,443**

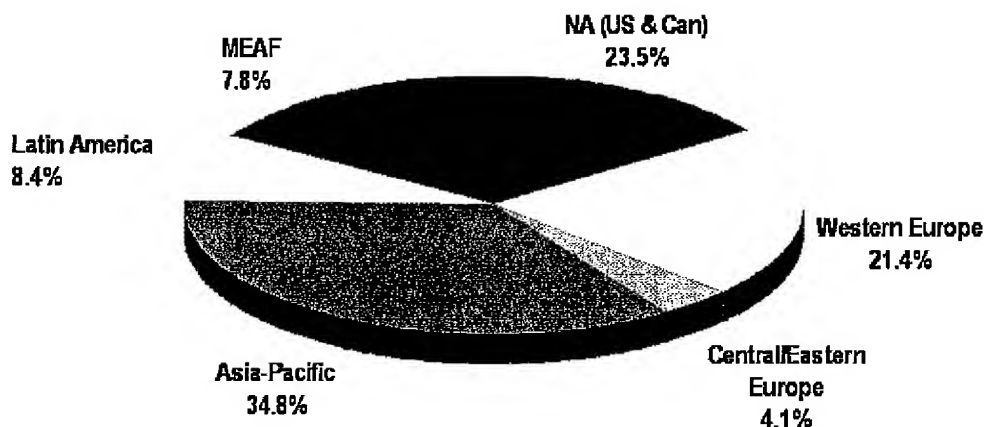
Polyethylene is the world's most widely used plastic, and linear low density polyethylene (LLDPE) is the fastest-growing type of polyethylene. LLDPE has wide ranging applications, e.g., film, injection molding, rotational molding and blow molding. About 51% of LLDPE is used in film worldwide, as can be seen below (see ref. 1):



In Brazil, the consumption of LLDPE film reached the level of 88% in 2006, as can be seen in the chart below (see ref. 2):



This polyethylene has established itself as the third major member of the global polyethylene business along with LDPE and HDPE. (see ref. 3). The following pie chart shows world consumption of LLDPE (see ref. 1):



Braskem is a Brazilian petrochemical company and the thermoplastic's production leader in Latin America. In 2006, became one of the 5 biggest private industrial companies in Brazil with an annual production de 1,154 Kton of polyethylene. LLDPE is one of the thermoplastics produced in Braskem and its annual production is around 360 Kton, with 80% of this volume with application on films.

There are four distinct types of polyethylene production: a high pressure process, and three low pressure processes based upon solution, slurry and gas phase technologies (see ref. 4). The high pressure process, which operates at pressures around 1,500-2,000 bar, produces the LDPE resin, which film product has high clarity. However, the high pressures equipment involved is expensive and specialized. Low pressure processes, typically operating below 100 bar, are more cost effective in terms of capital expenditure but require the aid of a catalyst to obtain economical polymerization and the required polyethylene product (see ref. 4). HDPE can be produced at slurry or gas phase processes as far as the LLDPE can be produced in solution or gas phase processes.

Traditionally, polyethylene has been classified by its density, which essentially defines its rigidity or strength. LDPE with a highly branched molecular structure was the first type developed with a plant starting up in the UK as early as 1939. Later with the advent of suitable catalysts, HDPE was introduced, having a linear structure with a few or no short chain branching (SCB). As market needs changed, a LLDPE variety was developed in the mid-1970s, having a linear molecular structure with the important distinction of SCB and narrow molecular weight distribution (MWD). LLDPE is stronger and tougher than LDPE and less expensive to be produced, which makes it an attractive replacement for LDPE in many applications (see ref. 4). Polyethylene can be

attractive replacement for LDPE in many applications (see ref. 4). Polyethylene can be classified by density ranges, as shown below (see ref. 5). The density of a solid material is measured dividing its mass per unit volume. And specifically, the density of polymer is the weight per unit volume of the material at 23°C (see ref. 6).

•LDPE - 0.910 -0.925 g/cm<sup>3</sup>

•LLDPE - 0.910 -0.925 g/cm<sup>3</sup>

•LMDPE - 0.926 -0.940 g/cm<sup>3</sup>

•HDPE Type III - 0.941 -0.965 g/cm<sup>3</sup>

HDPE is a homopolymer of ethylene with a linear molecular structure and high density. LDPE is also a homopolymer of ethylene but the molecules have a branched structure with both long chain branching (LCB) and SCB. It has a lower density as compared to HDPE, mainly due to the presence of SCB. LLDPE is a copolymer produced by copolymerizing ethylene with  $\alpha$ -olefins (1-butene, 1-hexene, 1-octene, etc.). It has a linear molecular structure, due to the absence of LCB, but has a lower density as compared to HDPE, due to the presence of SCB (see ref. 7). It has been found that SCB control the density but have little effect on the rheological properties (see ref. 8). It has also been observed that the length of the SCB is also instrumental in controlling the density, with a longer side chain resulting in lower density (see refs. 8 and 9).

LLDPE show a broad variation in their properties by changing the type and comonomer content and its distribution in the polymer chain (see ref. 10 and 11). The heterogeneity in the short chain branch distribution (SCBD), according to Usami *et al.* (see ref. 12), results from the existence of various kinds of active centres with different activity in the polymerizations with traditional high activity Ziegler-Natta catalysts. The SCBD is the distribution of comonomer (number of branches) over polymer chains of different lengths. When SCBD is narrow, comonomer is uniformly distributed across all polymer chains regardless of chain length. When the SCBD is broad, the amount of comonomer per chain is a strong function of chain length (see ref. 12). These parameters and also the molecular weight and MWD of the polymers, are dictated by polymerization chemistry and reaction conditions (see refs. 13 – 16).

The comonomer incorporation in LLDPE results in polymer chains irregularities (SCB) which modify the ability of crystallization. These SCBD can be measured by a technique called CRYSTAF which separates molecules according to their amount of SCB (see ref. 11). This technique is based on monitoring the crystallization of LLDPE solution and the concentration is measured during the crystallization. Figure 2 shows an

example of a SCBD of two different Ziegler-Natta polyethylenes, measured by CRYSTAF.

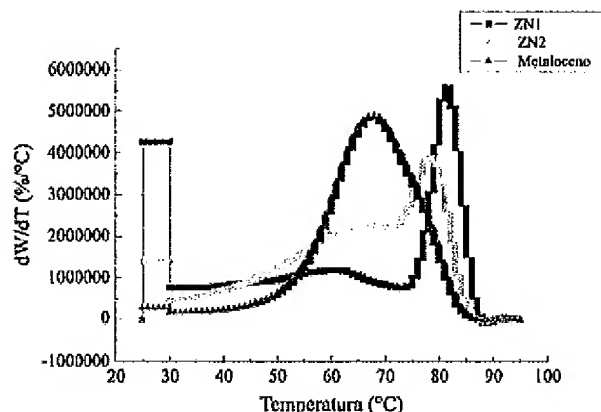


Figure 2 (from ref. 11)

When the temperature begins to decrease, the polymer fractions, which crystallized faster and are composed of molecules with little or no branches, will precipitate first, resulting in a decrease in the concentration of the solution. As the temperature decreases, fractions of macromolecules with the largest amount of short branches precipitate. The last fractions represent those polymers which remained soluble due to the low molecular weight and the high amount of SCB, i.e. a fraction soluble in xylene - XS (see ref. 11).

Depending upon catalyst type, reactor technology and process conditions, LLDPE with the same density can show different amounts of SCB and different SCBD. These differences can result in different properties as haze, gloss, blocking force, impact and puncture strength, melt fracture tendency, hot tack, hexane extractables and xylene soluble content (see refs. 17 – 19). Figure 1 shows the effect of density on LLDPE properties as gloss, haze, moisture barrier, etc. (see ref. 16).

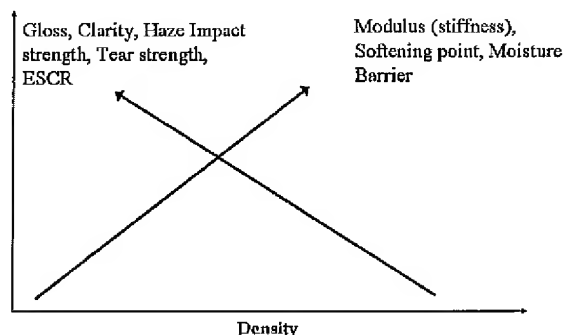


Figure 1 (from ref. 16)

High clarity polymer films produced from LDPE, LLDPE, PP, PVC and PET resins are inherently prone to blocking. Blocking is particularly common in films produced by the following techniques:

- Casting,
- Blown Film Extrusion,
- Biaxial Orientation,
- Calendaring,
- Etc.

Blocking is the adhesion between adjacent layers of film and may arise during processing, use and/or storage of the film. Blocking makes it difficult to open the tube after extrusion with, for example, blown polyethylene film. Blocking often occurs in tightly wound rolls of film; and reblocking occurs when sheets are stacked under some pressure and/or heat. Blocking and reblocking tendencies are measured as the force necessary to separate two layers of film after conditioning at a controlled temperature and/or pressure (see refs. 20 – 22).

Blocking can be related to the presence of low molecular weight polymer and/or low molecular weight polymer with high amount of SCB, i.e. the xylene soluble fraction from LLDPE polymers. As mentioned before, these fractions have a low crystallization point and are forced out of the crystalline regions during solidification of the extruded film, affecting the smoothness of the film's surface. An increase in the film's surface smoothness will cause adhesion between different film layers (see ref. 20).

The blocking force of film is generally considered unsatisfactory when it is about 20 g or more. To decrease blocking force, polyethylene manufactures incorporate additives (anti-block additives) into their polymers, which increase their productions costs and affect adversely optical and mechanical properties of the films (see ref. 23). Most anti-block additives increase the haze of polyethylene film, as can be seen in Figure 4 (see ref. 20).

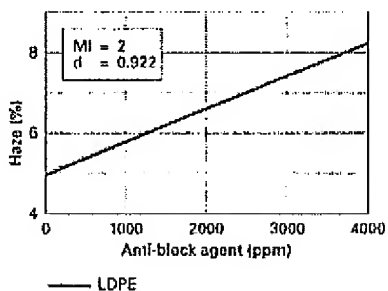


Figure 4 (from ref. 20)



One of the main uses of the LLDPE films is of food packaging application. Apart from its protective function, a packaging material should have a strong aesthetic appeal and optical properties are a key component. Often, packaging integrity and physical strength are achieved at the expense of optical properties. To satisfy the current consumer, the industry must provide “perfect” food with various qualities at the same time (nutrition, convenience, low calories, no fat, etc.) besides using packages that provide good storage, easy transportation and good visual in the food (see ref. 24). Consequently, in Brazilian market, they must be transparent to allow the visualization of the goods by the consumer. During processing, it is then necessary to optimize the properties of films such as gloss and haze (see refs. 25). Thus, the packaging is the factor that most influences the perception that the consumer has in relation to the product. If the consumer is not won by the pack, the product passes unnoticed or becomes fragile in the face of competition (see ref. 26).

Haze is the percentage of transmitted light that deviates by more than 2.5 degrees as a result of forward scattering by the film. Some polymers have much more inherent haze than others, and it is usual for haze to increase further with increasing film crystallinity or by the addition of an anti-block (see ref. 11 and 27). Gloss is a measurement of the proportion of the light striking a surface at a given angle, which is reflected at an equal and opposite angle. Gloss correlates with the shininess or sparkle of the surface. In other words, it is influenced by surface defects. To improve optical properties in a LLDPE film, is better to have a smaller amount of a high crystalline fraction which is composed of molecules with little or no SCB. Figure 5 shows the relation between haze and gloss in a LLDPE film. A film with good optical properties is the one which has low haze and high gloss (see refs 28 and 29).

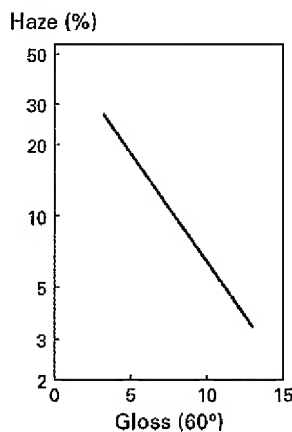


Figure 5 (from ref. 28)

Among the LLDPE grades produced in Braskem, all show density that are in the range of 0.917 a 0.920 g/cm<sup>3</sup> and melt flow index in the range of 0.55 a 2.3 g/10min (see ref. 30). The main applications for these grades are automatic packaging, high clarity films, heavy duty bag, stretch films, etc. Most of these applications require that the packaging, in the Brazilian market, present good appearance (good optical properties), low blocking force and good mechanical performance.

In Figure 6 is presented data for the application of the LLDPE in Brazilian market, as demand for segment, noting the fact that 90% of demand for LLDPE intended for the packaging industry (see ref. 31).

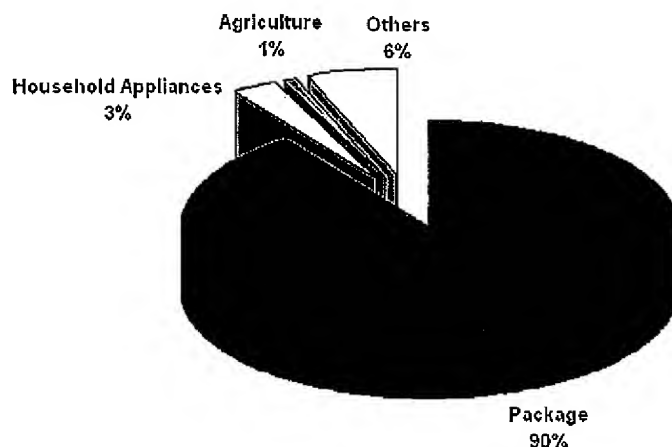


Figura 6 (from ref. 31)

To produce different kinds of polyethylenes as HDPE, LLDPE, LMDPE and LDPE, Braskem has gas phase, slurry, solution and high pressure processes. Among the processes using Ziegler-Natta catalysts (gas phase, slurry and solution), Braskem has two gas phase processes, from different licensors, producing several LLDPE grades and although both use catalysts derived from the same family, they are different in composition and also in their corresponding processes of preparation (see refs. 32 and 33). These two aspects as well as reactor technology and process conditions, can affect LLDPE properties showing different amounts of SCB and different SCBD, for the same polymer density and MW (or melt flow index). Another important aspect from these two gas phase processes, both requires that the catalyst and, consequently, the polymer, have good morphology (spherical), high bulk density (above 0.36 g/cm<sup>3</sup>) and very low fines polymer particles (below 1%) in order to avoid obstruction problems and fouling (see ref. 34). These fine particles tend to deposit onto and electrostatically adhere to the

inner walls of the reactor and heat exchanger, and to thereafter grow in size by chemical reaction thus causing an insulating effect and a lower heat transfer resulting in the formation of hot spots in the reactor (see ref. 34). As consequence a loss in fluidization efficiency and homogeneity generally occurs.

Therefore, it is crucial for the process that the catalyst used enables a total control of the polymer morphology resulting in product grains without fines, with high bulk density and good flowing properties.

The purpose of the present patent application Serial No. 10/518,443 was to develop a catalyst that meet all the requirements noted above, that is:

- The catalyst must have proper morphology adjust to one of Braskem gas phase process;
- The catalyst must produce a polymer with proper morphology adjust to one of Braskem gas phase process;
- The catalyst must produce a polymer with a bulk density equal to or greater than  $0.36 \text{ g/cm}^3$  necessary to be used in one of Braskem gas phase process;
- The catalyst must not produce fines polymer particles to avoid obstruction problems and fouling;
- The catalyst must produce LLDPE grades with density of  $0.917$  to  $0.919 \text{ g/cm}^3$  and a melt index of  $0.65$  to  $0.91 \text{ g/10 min}$ , which will be applied in Brazilian packaging market;
- The LLDPE grades with density of  $0.917$  to  $0.919 \text{ g/cm}^3$  and a melt index of  $0.65$  to  $0.91 \text{ g/10 min}$  must have a fraction soluble in xylene of equal to or less than  $10\%$  to avoid a high blocking force of films produced, i.e., blocking strength of  $15$  to  $30 \text{ g/100 cm}^2$ .
- The LLDPE grades must be able produce films with good optical properties as haze value of  $11.3$  to  $11.6\%$ , a gloss of  $79.3$  to  $80.7\%$  to satisfy the Brazilian consumer.

To satisfy all these requirements, the developed catalyst composition showed the following characteristics consisting essentially of:

- **Low amount of Titanium, Magnesium and Chlorine** (see Table 1 below):

Table 1

	Patent Application 0315-0158PUS1
Ti range (% w/w)	0.5 – 2.0
Mg range (% w/w)	0.3 – 3.0
Cl range (% w/w)	5.0 – 12.0

**- Substantially free of polar solvents in catalyst composition or during LLDPE production through ethylene copolymerization with one or more alpha-olefins.**

When you compare the catalyst composition of the present patent application Serial No. 10/518,443 with those from the three patents (EP 0522651 B1, EP 0480435 B1 and WO 91/08239) or even with commercial catalysts, it is possible to verify that these two requirements reached by the present patent application have not been met by the three patents or the commercial catalysts. To use a catalyst composition with higher amount of Titanium, Magnesium and Chlorine, as can be seen on those from patents EP 0522651 B1, EP 0480435 B1 and WO 91/08239 and from some commercial ones, to produce a LLDPE grade with density of 0.917 to 0.919 g/cm<sup>3</sup> and a melt index of 0.65 to 0.91g/10 min, and having a fraction soluble in xylene of equal to or less than 10% to avoid a high blocking force of films, is necessary to use an electron donor in catalyst composition or during ethylene copolymerization with one or more alpha-olefins. Some commercial Ziegler-Natta catalysts achieved a good LLDPE product (low xylene soluble content, good optical properties and low blocking) using a specific electron donor in catalyst composition or during ethylene copolymerization with one or more alpha-olefins.

Brita *et al.* in US patent 0,089,251 have claimed the production of a catalyst composition for the preparation of LLDPE which comprises Mg, Ti, halogen and an electron donor compound. They said that catalyst components display a homogeneous distribution of the comonomer in and among the copolymer chains. They also mentioned that heterogeneous Ziegler-Natta catalysts generally are not particularly satisfactory in doing so, and the general attempt is that of trying to improve these characteristics by using the so called electron donor compounds (see ref. 35).

Ko has showed the influence of the internal donor (ID) on molecular structure of LLDPE prepared with different Ziegler-Natta catalysts. He noticed that the xylene soluble value (XS) decreased by more than 50% with ID-added catalysts compared to that of no ID-added catalyst (see ref. 36). Figure 7 shows the effect of addition of ID on xylene soluble value of LLDPE produced and also the curve of dependency of polymer density and xylene soluble value.

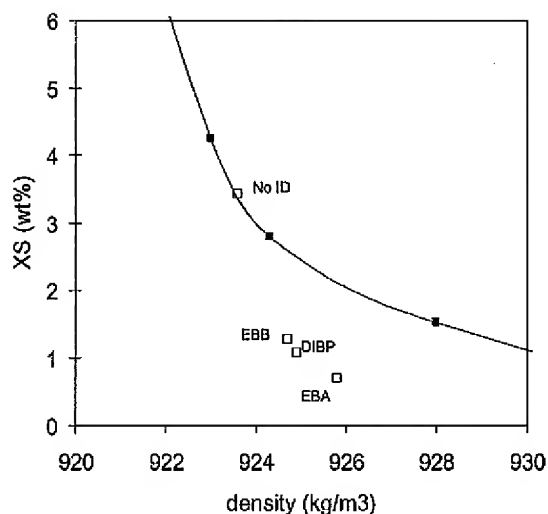


Figure 7 (from ref. 36)

However, some of the electron donors can suffer irreversible chemical reactions with aluminum alkyls compounds which are used on the preparation of the catalyst composition or during ethylene copolymerization with one or more alpha-olefins, as cocatalyst (see refs. 37 – 39). They can undergo a further reaction, especially in the presence of excess of aluminum alkyl, as is usual for polymerization. In the case of aromatic monoester, such as ethyl benzoate, a nucleophilic attack of free aluminum alkyl on the carbonyl group complexed with aluminum alkyl has been postulated. The reaction leads finally to the formation of two moles of dialkylaluminumalkoxide per one mole of ester, according to the following figure 8 (see refs. 37 – 39).

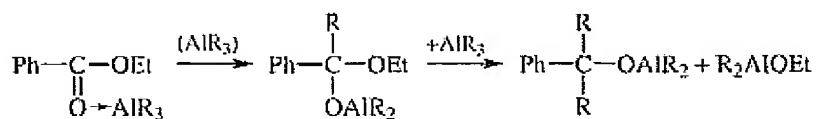


Figure 8 (from ref. 37)

In the case of the patents EP 0522651 B1 and EP 0480435 B1, even using an electron donor during the catalyst composition preparation, the amount of Titanium, Magnesium and Chlorine are higher and the comonomer response, i.e., the SCBD is broader compared to the comonomer response from the catalyst composition of the present patent application, as can be seen in Crystaf from figure 9. The soluble fraction which appears at temperature below 30°C, is higher for the LLDPE prepared with the catalyst composition of patent EP 0522651 B1 (example 1), which was reproduced in Braskem's

catalysis lab. The amount of this xylene soluble content was 14.2% compared to 9.7% of the LLDPE prepared with catalyst composition of example 8 of the present patent application Serial No. 10/518,443

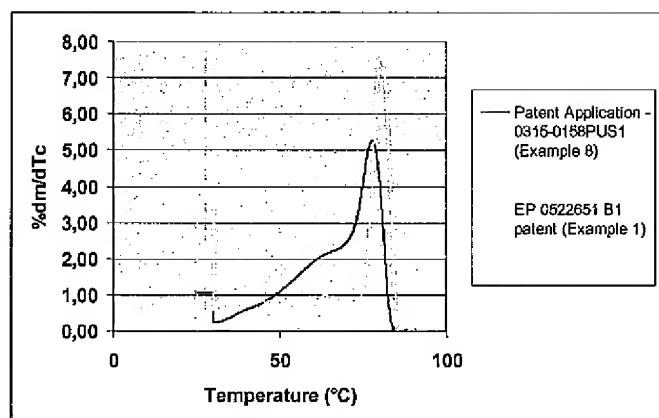


Figure 9

Some authors as Sindelar *et al.*, agree that higher concentration of titanium sites on silica supported catalysts can have different effect on activity and polyethylene properties when compared to catalyst compositions with smaller amounts of this active sites (see ref. 40).

Other requirements to use catalysts in copolymerization at gas phase processes as, bulk density equal to or greater than  $0.36 \text{ g/cm}^3$ , fines polymer particles content less than or equal to 1% to avoid obstruction problems and fouling, were not achieved by the catalyst compositions of the three patents (EP 0522651 B1, EP 0480435 B1 and WO 91/08239) which were reproduced in Braskem's catalysis lab and the results are listed in Table 2 below:

Table 2

Comparative Test Number	TEST 1	TEST 2	TEST 3	TEST 4	TEST 5	TEST 6	TEST 7	TEST 8
Product	LLDPE	LLDPE	LLDPE	LLDPE	LLDPE	LLDPE	LLDPE	LLDPE
Catalyst from	EP 0522651 B1 patent (Example 1)	EP 0522651 B1 patent (Example 4)	EP 0480435 B1 patent (Example 3)	EP 0522651 B1 patent (Example 1)	WO 91/08239 patent (Example 10)	WO 91/08239 patent (Example 10)	WO 91/08239 patent (Example 10)	Patent Application - 0315-0158PUS1 (Example 8)
Ti (%w/w)	6.8	5.2	5.6	6.8	3.9	3.9	3.9	2.0
Mg (%w/w)	2.7	3.4	2.3	2.7	1.9	1.9	1.9	1.5
Aluminum alkyl	TEAL	TEAL	TEAL	TEAL	TEAL	TEAL	TEAL	TEAL
Ethylene partial pressure (bar)	5	5	5	5	5	5	5	5
Temperature (°C)	75	75	75	75	75	75	75	75

Time (h)	3	3	3	3	3	3	3	3
Al/Ti	300	300	300	300	300	300	300	300
Butene-1 (L)	0.29	0.29	0.29	0.7	0.29	0.7	1.1	0.29
H <sub>2</sub> /C <sub>2</sub> molar ratio	0.47	0.47	0.40	0.40	0.47	0.40	0.35	0.40
Bulk Density (g/cm <sup>3</sup> )	0.26	0.30	0.27	0.29	0.30	0.31	N.A.	0.36
Fines (%)	N.A.	3.0	2.8	2.2	1.5	1.7	N.A.	0.1
MFI (2,16) (g/10')	1.00	1.30	0.40	1.34	0.29	1.25	1.30	0.91
Butene content (% w/w)	5.7	6.7	4.7	9.7	5.5	N.A.	N.A.	8.7
Density (g/cm <sup>3</sup> )	0.938	0.925	0.928	0.918	0.925	0.923	N.A.	0.917
Xylene soluble (% w/w)	5.3	7.3	6.9	14.2	3.0	5.2	N.A.	9.7

N.A. = not analyzed

## CONCLUSIONS

Summarizing this report, catalysts composition from the present patent application showed the following characteristics consisting essentially of:

- Low amount of Titanium, Magnesium and Chlorine
- Substantially free of polar solvents in catalyst composition or during LLDPE production through ethylene copolymerization with one or more alpha-olefins.

These characteristics have not been met by the three patents (EP 0522651 B1, EP 0480435 B1 and WO 91/08239).

With these catalysts compositions Braskem is able to produce LLDPE grades with density of 0.917 to 0.919 g/cm<sup>3</sup> and a melt index of 0.65 to 0.91g/10 min in one of its gas phase process achieving the following requirements:

- Good morphology adjusts to one of Braskem gas phase process;
- Polymer with proper morphology adjusts to one of Braskem gas phase process;
- Polymer with a bulk density equal to or greater than 0.36 g/cm<sup>3</sup> necessary to be used in one of Braskem gas phase process;
- Low amount of fines polymer particles to avoid obstruction problems and fouling (< 1%);

- LLDPE grades applicable in Brazilian packaging market;
- LLDPE grades with fraction soluble in xylene of equal to or less than 10% to avoid a high blocking force of films produced, i.e., blocking strength of 15 to 30 g/100 cm<sup>2</sup>.
- LLDPE to produce films with good optical properties as haze value of 11.3 to 11.6%, a gloss of 79.3 to 80.7% to satisfy the Brazilian consumer.



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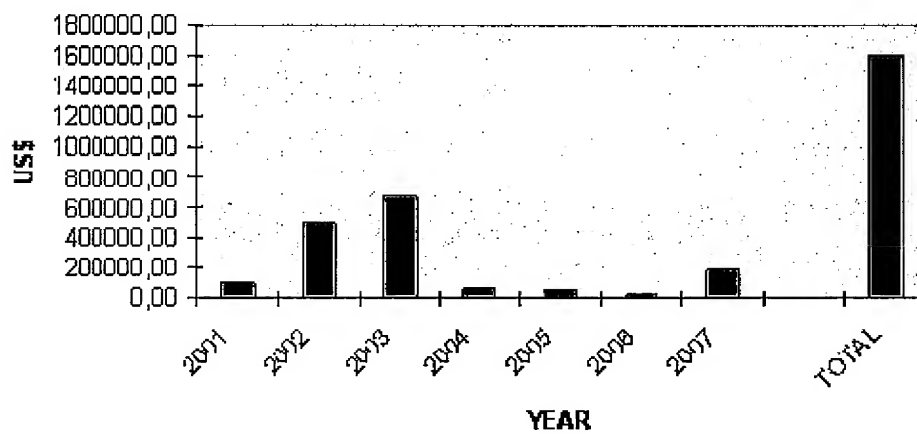
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## APPENDIX 2

### POTENTIAL COMMERCIAL SUCCESS OF THE CATALYST DEVELOPMENT FOR GAS PHASE POLYMERIZATION PLANT

The amount of money spent until 2007 can be seen in the graph below and we've already spent around US\$ 1.6 MM.

**CATALYST DEVELOPMENT INVESTMENT**



What we need to spend until the project is concluded is around US\$ 3 MM (Pilot Plant and Industrial tests).